ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR STUDYING DSSC ELECTROLYTES

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Abstract. Dye-sensitized solar cells (DSSCs) rely critically on the electrolyte to regenerate the dye, transport redox species, and sustain charge-transfer at the counter electrode while limiting recombination at the photoanode interface. Electrochemical impedance spectroscopy (EIS) is one of the most informative nondestructive methods for separating bulk electrolyte transport from interfacial kinetics and diffusioncontrolled processes across a broad frequency window. This review consolidates the theoretical basis of impedance spectroscopy in forms directly usable for DSSC electrolyte research, with emphasis on Nyquist/Bode interpretation, constant-phase behavior, diffusion impedance, and the relationship between fitted parameters and physically meaningful electrolyte properties such as ionic conductivity, effective permittivity, diffusion coefficient, mobility, and charge-carrier concentration. We provide a rigorous and practical workflow for designing EIS experiments in symmetric "dummy" cells and complete DSSCs under dark and illumination, highlight pitfalls related to non-stationarity and model non-uniqueness, and describe validation using Kramers-Kronig consistency tests. Representative electrolyte formulations-including iodide/triiodide liquid electrolyte and gel polymer electrolytes based on PAN/EC/PC with iodide salts and ionic-liquid iodides, as well as polymer blends such as PVP/PMMA-are discussed to illustrate how composition and morphology impact impedance signatures. The review closes with reporting recommendations aimed at improving reproducibility and comparability across studies, enabling EIS-guided electrolyte optimization toward higher efficiency and improved stability DSSCs [1,2].

Keywords: DSSC; electrolyte; electrochemical impedance spectroscopy; Nyquist plot; Bode plot; gel polymer electrolyte; iodide/triiodide; diffusion impedance; constant phase element; Kramers-Kronig validation

Nomenclature: Z impedance; Z_r real part; Z_i imaginary part; ω angular frequency; τ time constant; R resistance; R_s series resistance; R_{ct} charge-transfer resistance; C capacitance; ε_r relative permittivity; ε_0 vacuum permittivity; S area; d thickness; σ ionic conductivity; D diffusion coefficient; μ mobility; n carrier concentration; e elementary charge; k_B Boltzmann constant; T absolute temperature

INTRODUCTION

Since the seminal demonstration of the modern DSSC architecture using mesoporous TiO_2 films, the electrolyte has been recognized as a decisive component controlling charge transport, redox turnover, interfacial charge transfer at the counter electrode, and long-term operational stability. Nature In the classical DSSC, the electrolyte provides (i) dye regeneration via the redox mediator, (ii) diffusion of oxidized/reduced species between electrodes, and (iii) ionic screening and interfacial structuring that can modify recombination dynamics at the TiO_2 /electrolyte interface. Electrolyte composition therefore influences current generation, photovoltage, fill factor, and device ageing.

Electrochemical impedance spectroscopy (EIS) has become a standard diagnostic in DSSC research because it can separate multiple processes that occur simultaneously during operation. A widely used DSSC impedance framework assigns high-frequency features to the counter electrode and ohmic contributions, intermediate-frequency features to electron transport/recombination in the photoanode, and low-frequency features to diffusion in the electrolyte. Beyond qualitative interpretation, EIS enables quantitative extraction of resistive, capacitive, and diffusional parameters that can be linked to electrolyte transport (ionic conductivity, diffusion coefficients) and kinetics (charge-transfer resistances). For publicationgrade claims, however, careful protocol design, data validation, and transparent modeling are essential. EIS tutorials and methodological guidance stress that impedance interpretation is only valid when the measured system is linear, causal, and stable during the measurement, and they recommend Kramers-Kronig (K-K) tests to verify data quality[3].

This review focuses specifically on DSSC electrolytes and how EIS can be used to (i) quantify bulk transport in liquid and gel polymer electrolytes, (ii) separate electrolyte diffusion from interfacial charge transfer, and (iii) understand electrolyte-driven changes in recombination and ageing behavior in complete DSSCs.

DSSC electrolytese. In a DSSC, photons excite the dye, electrons are injected into TiO_2, and the oxidized dye must be reduced back to its ground state by the redox mediator in the electrolyte. The oxidized mediator then diffuses to the counter electrode, where it is reduced, completing the circuit. Any limitation in electrolyte diffusion or ionic conduction produces additional overpotentials and manifests as characteristic lowfrequency impedance. At the same time, electrolyte ions structure the interfacial region at the photoanode, affecting band-edge shifts and recombination kinetics, which appear in the intermediatefrequency impedance response.

Liquid iodide/triiodide electrolytes remain a benchmark because they support efficient dye regeneration and relatively fast diffusion. Nevertheless, leakage, evaporation, and thermal/photochemical stability concerns motivate quasi-solid approaches (gel polymer electrolytes, ionic-liquid gels) that immobilize solvent while

maintaining acceptable ionic transport. Broad reviews on gel polymer electrolytes for DSSCs highlight that maintaining high ionic conductivity while improving mechanical stability is a central challenge, commonly addressed by polymer blending, plasticizers, ionic liquids, and functional additives[3,4].

Impedance spectroscopy theory for electrolyte systems in DSSCs

EIS applies a small sinusoidal perturbation and measures the system response as a function of frequency. If the applied voltage is

$$V(t) = V_0\sin(\omega t) \tag{1}$$

and the current response is

$$I(t) = I_0\sin(\omega t + \theta) \tag{2}$$

then the impedance is defined in the frequency domain as

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = Z_0(\omega)e^{-j\theta(\omega)} \tag{3}$$

The complex impedance is commonly written as

$$Z(\omega) = Z_r(\omega) - jZ_i(\omega) \tag{4}$$

where Z_r and Z_i are the real and imaginary components, respectively, and $j = \sqrt{-1}$. Using magnitude Z_0 and phase θ,

$$Z_r = Z_0\cos(\theta), Z_i = Z_0\sin(\theta) \tag{5}$$

In Nyquist coordinates, impedance is plotted in the complex plane, most commonly Z_r on the x-axis and $-Z_i$ on the y-axis (sign convention varies). Each point corresponds to a frequency [5]. In Bode plots, $|Z|$ and θ are plotted versus frequency. For DSSCs, using both representations helps assign processes: semicircles and arcs in Nyquist plots often correspond to phase peaks in Bode plots.

3.3. Non-ideal capacitive response and constant phase elements

Electrolyte-containing electrochemical systems often deviate from ideal capacitor behavior due to electrode roughness, porous microstructure, distributed relaxation times, and heterogeneity in gels. A widely used phenomenological element is the constant phase element (CPE), written as

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^p} \tag{6}$$

where Q is a pseudo-capacitance parameter and $0 < p \le 1$ (with $p = 1$ representing an ideal capacitor). Power-law dispersion is also used directly to express real and imaginary parts of impedance for certain electrolyte polarization models. Your provided expressions (series resistance plus a dispersive term) can be written as

$$Z_r = R + \frac{\cos\left(\frac{\pi p}{2}\right)}{k^{-1}\omega^p}, Z_i = \frac{\sin\left(\frac{\pi p}{2}\right)}{k^{-1}\omega^p} \tag{7}$$

In practice, parameter identifiability requires (i) sufficient frequency coverage, (ii) stable spectra, and (iii) model parsimony, because different circuits can fit similar arcs.

A widely cited DSSC EIS framework attributes:

(i) high-frequency response to series resistance and counter-electrode charge-transfer resistance;

(ii) intermediate-frequency response to electron transport and recombination at the TiO_2 /electrolyte interface (often represented via recombination resistance and chemical capacitance);

(iii) low-frequency response to diffusion of redox species in the electrolyte.

This assignment is supported by influential DSSC impedance analyses and is consistent with the theoretical modeling of DSSC frequency response. More general solar-cell impedance theory also provides a physics-based context for interpreting capacitive and transport phenomena in electrochemical photovoltaics [6].

When the primary goal is electrolyte transport (conductivity and diffusion), symmetric "dummy" cellssuch as Pt | electrolyte | Pt-are often the most interpretable configuration. They reduce the complexity introduced by mesoporous TiO_2 electron transport and recombination. Studies of gel polymer electrolytes commonly use symmetric cells explicitly for EIS-based extraction of transportrelated parameters.

Complete DSSCs

Electrolyte changes can modify counter-electrode kinetics, recombination resistance, and chemical capacitance-effects that matter directly for device performance and stability. Therefore, a robust electrolyte paper typically includes both (i) symmetric-cell EIS for transport/kinetics isolation and (ii) complete-device EIS under relevant operating conditions (dark bias and/or illumination at open circuit). Classical DSSC EIS analysis explicitly connects spectral features with counter-electrode charge transfer, TiO_2 transport and recombination, and electrolyte diffusion.

Electrolyte diffusion processes can require low frequencies, whereas interfacial charge transfer often appears at higher frequencies. The chosen frequency window should span all relevant arcs and tails. The perturbation must be small enough to preserve linear response [7].

EIS interpretation is only reliable if the system remains stable during the measurement. Drift (due to temperature changes, slow interfacial evolution, or illumination-induced changes) can distort low-frequency features. EIS tutorials emphasize the role of Kramers-Kronig (K-K) relations to evaluate data quality; if data are linear, causal, and stable, they should satisfy K-K consistency within reasonable approximations.

A practical validation workflow recommended in EIS guidance documents includes:

(i) repeating spectra to check overlap;

(ii) monitoring open-circuit potential before/after long scans;

(iii) applying $K - K$ tests to detect non-physical spectra;

(iv) reporting validation outcomes and fit residuals.

Parameter extraction: conductivity, permittivity, diffusion, mobility, concentration This section rewrites and standardizes the parameter relations you provided, using publication-style mathematical form.

For an electrolyte layer of thickness d and area S, an effective capacitance can be written as

$$C = k^{-1} = \frac{\varepsilon_r \varepsilon_0 S}{d} \tag{8}$$

Here ε_r is the electrolyte relative permittivity and ε_0 is the vacuum permittivity.

If R is the active (ohmic) resistance associated with the electrolyte layer in a defined geometry, ionic conductivity can be estimated as

$$\sigma = \frac{d}{RS} \tag{9}$$

A characteristic time constant can be associated with a characteristic angular frequency ω :

$$\tau = \frac{1}{\omega} \tag{10}$$

The specific feature used to define ω should be stated explicitly (e.g., frequency at a phase peak, arc apex, or another model-defined extremum).

A simplified estimate for the diffusion coefficient is

$$D = \frac{d^2}{\tau} \tag{11}$$

Using the relation

$$d = k \varepsilon_r \varepsilon_0 S \tag{12}$$

one obtains

$$D = \frac{(k \varepsilon_r \varepsilon_0 S)^2}{\tau} \tag{13}$$

Charge-carrier mobility is linked to diffusion by

$$\mu = \frac{eD}{k_B T} \tag{14}$$

giving

$$\mu = \frac{e(k \varepsilon_r \varepsilon_0 S)^2}{k_B T \tau} \tag{15}$$

Carrier concentration from conductivity
Using

$$\sigma = n \mu e \tag{16}$$

the concentration is [8]

$$n = \frac{\sigma k_B T \tau}{e^2 (k \varepsilon_r \varepsilon_0 S)^2} \tag{17}$$

Electrolyte preparation routes used as case examples for EIS analysis This section uses your provided recipes as representative formulations and connects them to expected impedance signatures. A representative liquid electrolyte can be prepared by dissolving

iodine in ethylene glycol, followed by adding potassium iodide and stirring until homogeneous. Such iodide/triiodide electrolytes remain central in DSSC literature and provide a practical benchmark for comparing gel systems.

EIS expectations: relative to low-viscosity solvents, ethylene glycol increases viscosity, which tends to enhance diffusion impedance and shift diffusion-associated characteristic frequencies lower. In symmetric Pt | electrolyte | Pt cells, one typically observes an ohmic intercept, a charge-transfer feature at higher frequency (counter-electrode kinetics), and a diffusion-controlled feature at lower frequency.

PAN-based gel electrolytes for DSSCs are widely studied, including systematic selection of iodide salts and the use of symmetric Pt cells for EIS characterization.

EIS expectations in gels: compared with liquids, gelation often increases bulk resistance and strengthens dispersive (CPE-like) behavior due to polymer heterogeneity and electrode polarization. However, carefully designed PAN-based gels can achieve high ionic conductivity while improving mechanical stability, and EIS is routinely used to quantify the conductivity and charge-transfer/diffusion contributions.

Second polymer-based electrolyte dissolves iodide salt (TBAI or KI) in DMSO at elevated temperature and then adds PVP and PMMA (2:1), mixing until gelation. Polymer blends are commonly used to tune mechanical strength and segmental dynamics, often increasing non-ideal capacitive dispersion in EIS. Recent gel-electrolyte studies continue to explore PVP-containing gels and their interfacial dynamics in DSSCs [9,10,11].

CONCLUSIONS

EIS provides a uniquely powerful route to study DSSC electrolytes because it can disentangle bulk transport (ionic conductivity, diffusion-related impedance) from interfacial kinetics (counter-electrode charge transfer) and from electrolyte-driven changes in recombination/chemical capacitance in complete devices. Classical DSSC EIS studies established widely used frequency-domain assignments and modeling approaches, while modern EIS methodology emphasizes data validity (linearity, causality, stability) and the importance of Kramers-Kronig checks. For electrolyte engineeringparticularly when moving from liquid to gel polymer electrolytes such as PAN/EC/PC systems with iodide salts and ionic-liquid iodides-EIS can quantify how composition and microstructure alter conductivity, dispersion, diffusion limitations, and interfacial resistances. By adopting rigorous experimental design, validation, and transparent reporting, EIS-based electrolyte studies can meet the standards expected by high-quality journals and accelerate rational optimization of stable, efficient DSSCs.

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